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Reports
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WOOD CHEMISTRY LABORATORY

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A REPORT SUBMITTED TO THE FOREST SERVICE

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INTRODUCTION

The DuPont Model 916 Thermal Evolution Analyzer (TEA) diagrammed in Fig. 1, uses a flame ionization detector (FID) to measure carbon evolved as a sample is heated, either isothermally or at a programmed rate. The response of the FID corresponds to the rate of evolution of combustible carbon; the integrated response gives the total combustible carbon evolved to a given temperature. The TEA has been proposed as a convenient method for measuring the heat release as a function of temperature from forest fuels, using the relationship between carbon content and heat of combustion of natural fuels and their pyrolysis products, which was developed under a cooperative agreement between the Northern Forest Fire Laboratory and the Wood Chemistry Laboratory of the University of Montana.

In the previous study the heat of combustion and carbon content of the volatile fraction were determined by difference from elemental and calorimetric analyses of the fuel and its char. Because of the extensive analysis necessary in this method, volatile products were not differentiated between temperature ranges, but summed over the entire range from room temperature to 400°. The TEA can be evaluated by comparison of the results of that study with equivalent TEA results for the same fuel samples.

EXPERIMENTAL METHODS

Samples for analysis (700-800 μg) were weighed to the nearest microgram on a Cahn R-100 electrobalance equipped with a digital voltmeter, and heated under flowing nitrogen (30 ml/min) from room temperature to 400° at

a rate of 16°/min. The detector response was recorded simultaneously as a function of temperature on a DuPont Model 990 Thermal Analyzer and as a function of time on a recorder equipped with a disc integrator. The integrated response was calibrated in terms of integrator counts per microgram carbon using inositol ($C_6H_{12}O_6$), which melts and vaporizes above 220° without decomposing, so all of the carbon is detected. In order to reduce errors due to variable gas flows, standards were run at least twice daily and the hydrogen and air flows were checked before each run with a bubble flowmeter.

The moisture content of the fuel sample was checked by thermogravimetry (TG) using the Cahn R-100 electrobalance equipped with a tube furnace programmed at 15°/min by the thermal analyzer. The percent water was calculated on a dry weight basis from the percent weight loss at 125°. The TEA results were converted to a dry weight basis using this data.

The mass balance data were obtained as described previously.[1] Compensation must be made for the different sample sizes used in the two studies, since the percent char is greater for larger sample sizes. Therefore, the mass balance results obtained using 1 g samples were recalculated using the percent char obtained for 2 mg samples by TG, assuming the elemental analysis of the char was the same.

DISCUSSION OF RESULTS

The TEA results for the dead fuels are given in Table I, and graphically compared with the mass balance data in Figure 2. The standard deviation of 14.9% is within the acceptable range for these studies in view of the convenience of the method, the added capability of determining the temperature dependence of combustible gas evolution, and the ability to

analyze larger sets of samples. Since the samples in the original study were selected to provide wide variation in the content of several constituents, they represent an extreme test for the TEA method. Close analysis of the deviations between the data sets suggests both shortcomings in the TEA method and a means of improving it.

The response of the flame ionization detector to organic carbon is linear within a given class of compounds, but varies for carbon atoms attached to different functional groups.[2-4] Generally, the response decreases as the carbon becomes more oxidized. Since pyrolysis of cellulosic fuels and evaporation of the volatile oils produce a wide variety of compounds, accurate determination of the carbon evolved depends on an averaging of the level of oxidation among the volatile products between fuel samples and throughout the entire temperature range.

Previous studies, using both hardwoods and softwoods, have shown that the heats of combustion of the volatiles generated over several stages of decomposition are nearly constant.[5-7] One can thus infer that the level of oxidation of the volatile compounds is constant because of the equivalence of heat of combustion and carbon content. Roberts reported that the elemental composition of the volatiles can be represented by $(CH_2O)_n$, indicating that inositol would be a good calibration standard, since it has the same composition.[8] The data given in Figure 2 for woody samples seems to verify Roberts' results, since the values obtained by mass balance and TEA using inositol as a standard compare well. For samples other than the woody tissues, the comparison becomes less precise.

Cellulose, which initially has the same elemental composition as the

standard produces more highly oxidized volatiles in charring. The greater level of oxidation is manifested in the lower evolved carbon value obtained by TEA due to the lower response of the FID to these highly oxidized compounds. At the other extreme is aspen foliage, which is known to contain high concentrations of compounds extractable with nonpolar solvents. These nonpolar components which have greater response per unit weight of carbon cause the TEA value to be significantly higher than the mass balance value.

In order to determine the magnitude of error possible with the inositol standard, a sample of camphor ($C_{10}H_{14}O$), a representative of the extractive components, was run on the TEA and compared with a sample of inositol run under the same conditions. The response of the FID to inositol was 65% that of camphor, indicating that analysis by TEA using inositol as a standard could give results 50% higher than the actual value, although it is likely that most of the extractives would have a higher degree of oxidation than camphor.

The level of oxidation of the volatiles varies between different temperature ranges according to their chemical composition. Low molecular weight compounds having a lower degree of oxidation than the carbohydrates, e.g., the terpenes, are likely to evaporate without decomposing at low temperatures. At higher temperatures the decomposition of the lignin would produce volatiles of approximately the same composition as the cellulose decomposition products. The decarboxylation of the char at higher temperatures[9,10] will be undetected, resulting in slight deviations from the mass balance results. Since these gasses are not combustible, however, they are important only in terms of their contribution to the average

level of oxidation of the volatile fraction, and the TEA data reflects the heat release more accurately than mass balance methods in this temperature range. These errors should have a cancelling effect over the entire temperature range, but the heat release within each temperature range will not necessarily be accurate.

FUTURE PLANS

The TEA method will continue to be evaluated and improved. The most significant problem is in achieving accurate calibration over wide temperature ranges. For more accurate analysis, a calibration factor might be used to adjust for changes in the chemical composition of the volatiles within each temperature range. The correction would be complicated by changes in the chemical composition of the fuel, however, and would be unsatisfactory in most cases.

A better approach might be to use a different detection system. One detector which will be evaluated is the reaction coulometer. This detector combusts evolved carbon completely, generating the stoichiometric amount of oxygen necessary for the combustion. The response is equivalent to the current required for the electrolytic generation of the oxygen. This method will not be quantitative for the amount of carbon evolved, but the oxygen consumption should correspond very closely to the heat of combustion of the evolved gasses. Thus, the desired parameter is measured directly. Preliminary studies have shown that this method will be accurate to within approximately 6% over all temperature ranges. This could represent a significant improvement over flame ionization detection, both in terms of total heat determination and the relative evolution with temperature intervals.

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Table 1. Comparison of TEA and Mass Balance Results from Dead Forest Fuels.

Sample	Combustible Carbon Evolved to 400° (μg C/μg fuel)[a]		Deviation[b] (%)
	Determined by TEA	Determined by Mass Balance	
Cellulose (1)[c]	0.322	0.377	17.1
Excellsior (2)	0.318	0.350	10.1
Larch Wood (3)	0.279	0.286	2.5
Punky Wood (4)	0.257	0.206	19.8
Chamise Stems (5)	0.246	0.213	13.4
Fourwing Saltbush Stems (6)	0.236	0.216	8.5
Castlevalley Saltbush Stems (7)	0.218	0.211	3.2
Creeping Sage (8)	0.257	0.222	13.6
Ponderosa Pine Needles (9)	0.300	0.251	16.3
Aspen Leaves (10)	0.328	0.231	29.6
Chamise Foliage (11)	0.267	0.209	21.7
Fourwing Saltbush Foliage (12)	0.208	0.200	3.8
Castlevalley Saltbush Foliage (13)	0.154	0.156	1.3

[a] Based on the dry weight of fuel.

[b] Based on TEA value.

[c] Numbers refer to points in Fig. 2.

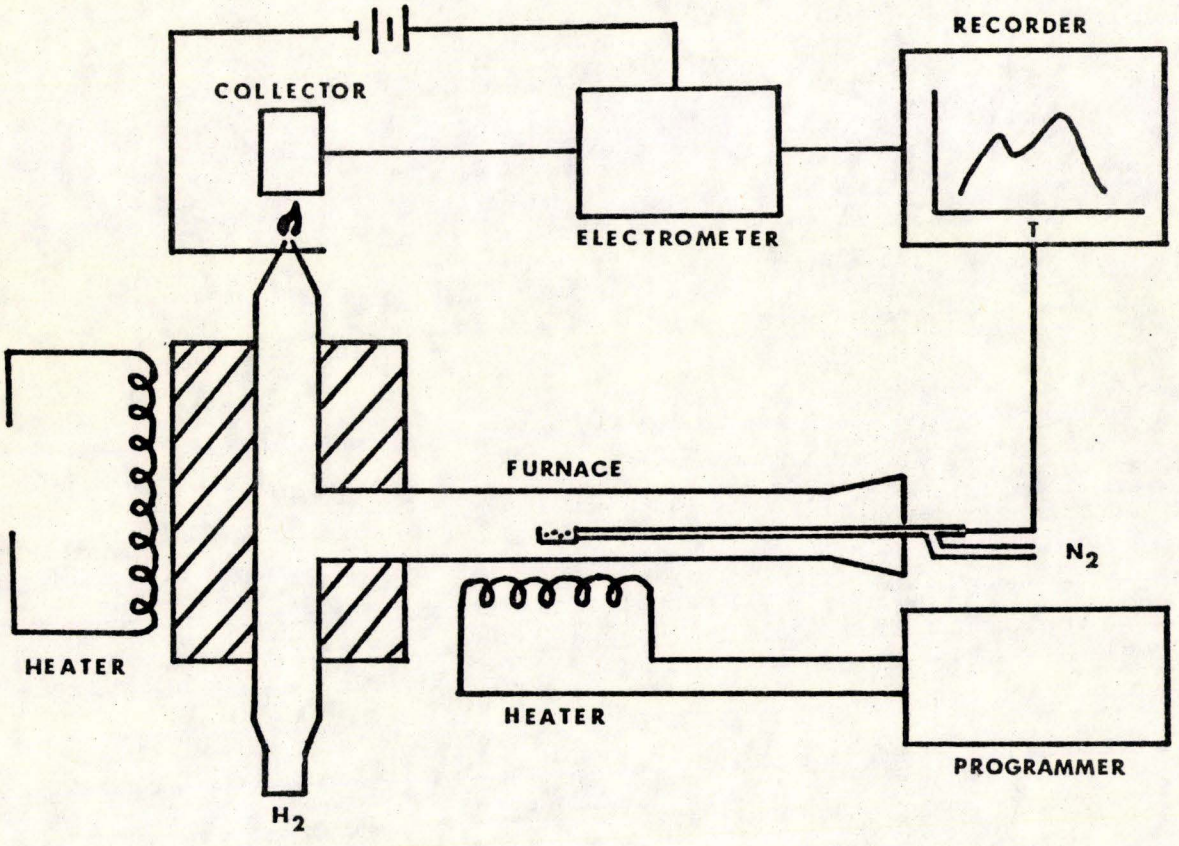

Fig. 1. Block diagram of the Thermal Evolution Analysis system.

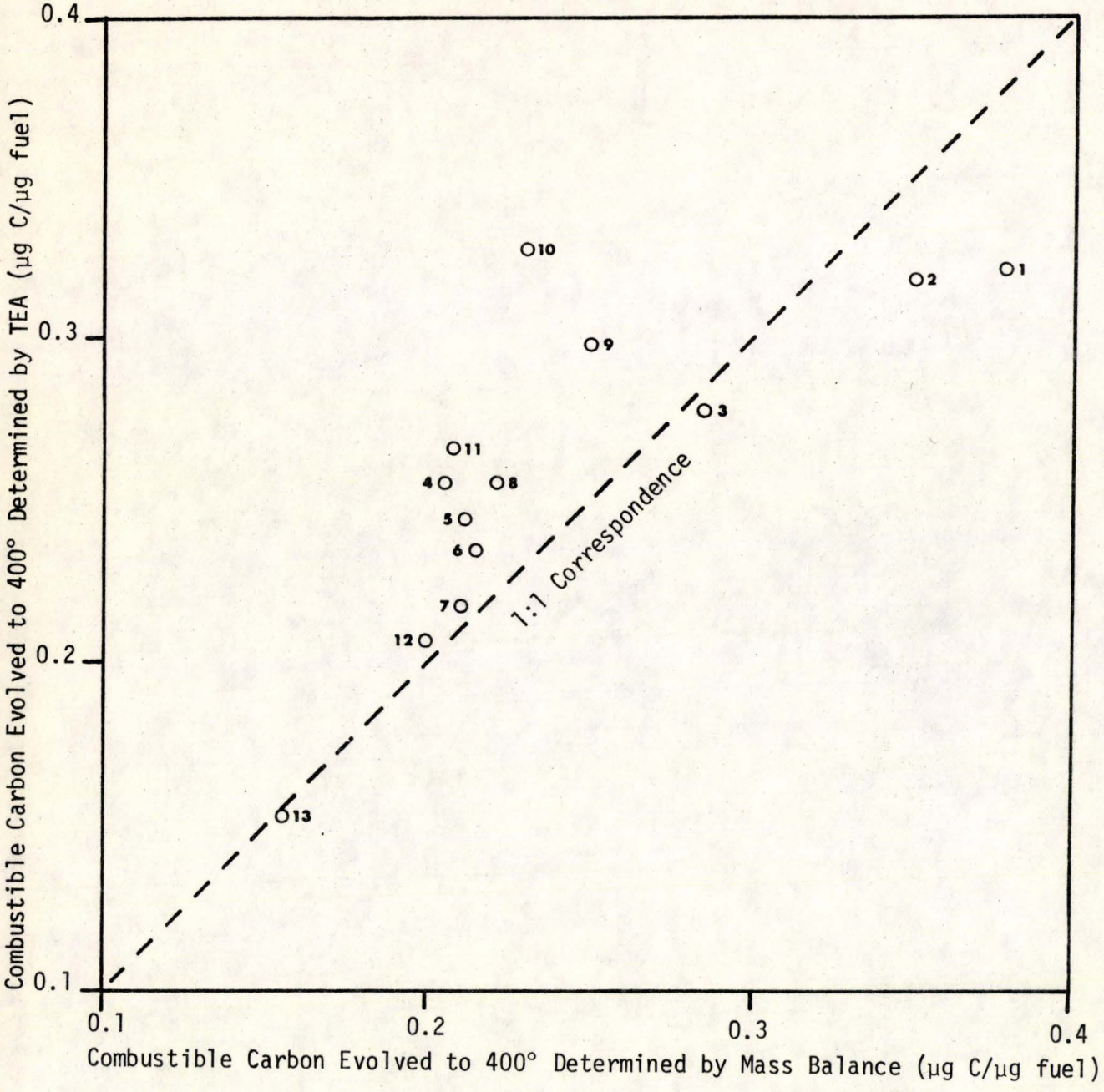

Figure 2. Comparison of TEA and mass balance results from dead forest fuels (samples identified according to numbers in Table 1.